

**DEVELOPMENT OF LITHIUM/METAL SULFIDE BATTERIES
AT ARGONNE NATIONAL LABORATORY:
SUMMARY REPORT FOR 1977**

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March 1978

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PREFACE

This report is a summary of the accomplishments during 1977 in Argonne National Laboratory's program on high-temperature secondary batteries. This work is carried out at Argonne, primarily in the Chemical Engineering Division, and at the laboratories of various industrial subcontractors. The major subcontractors during 1977 were the Atomics International Division of Rockwell International, the Carborundum Co., Catalyst Research Corp., Eagle-Picher Industries, Inc., and Gould Inc. Some of the efforts of the many scientists, engineers and technicians who have contributed to this program during the year are reflected in the list of publications at the end of this report, and in other publications planned for the near future. Although acknowledgment of the contributions of individuals is beyond the scope of this brief report, their efforts are essential to the success of the program.

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DEVELOPMENT OF LITHIUM/METAL SULFIDE BATTERIES
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ABSTRACT

This report consists of highlights for 1977 of Argonne National Laboratory's program on the development of lithium/metal sulfide batteries. The intended applications for these high-performance batteries are electric-vehicle propulsion and stationary-energy-storage applications such as load-leveling on electric-utility systems. The battery cells consist of a lithium-aluminum or lithium-silicon alloy negative electrode, an FeS or FeS₂ positive electrode, and a molten LiCl-KCl electrolyte, which requires an operating temperature of 400-450°C. Most of the cells tested during the year were of a prismatic design, with capacities in the range of 100-200 A-hr.

In 1977, subcontracts were continued with three industrial firms on the development of cell fabrication techniques and the fabrication of cells for testing either at Argonne or in their own laboratories. Industrial subcontracts were also continued on the development and fabrication of electrical feedthroughs and electrode separators. In addition, the Atomics International Division of Rockwell International continued a more general research and development effort on lithium-silicon/iron sulfide batteries under a subcontract with Argonne. These contracts have proved to be an effective means of transferring battery technology to industry, as well as bringing industrial expertise into the program.

As a result of the Electric and Hybrid Vehicle Research, Development and Demonstration Act of 1976, increased emphasis has been placed on the development of the electric-vehicle battery. In November 1977, proposals were solicited for the development, design, and fabrication of a 40 kW-hr battery to be tested in an electric van at ANL early in 1979. After testing the 40 kW-hr battery, electric-vehicle batteries with higher performance, longer lifetime, and potentially lower cost in mass production will be fabricated.

Conceptual designs for a 6 MW-hr battery module for stationary energy storage have been completed both at Argonne and at Atomics International. Both versions involve cells of about 4 kW-hr capacity, which are to be assembled into submodules. Testing of a battery module in the BEST (Battery Energy Storage Test) Facility is expected to take place in 1983.

Nearly 200 cells were fabricated by industrial subcontractors in 1977 for testing at Argonne or in their own laboratories; approximately 45 additional cells of various designs were fabricated and tested at Argonne to evaluate different types of electrodes, current collectors, separators, and other cell components.

Work was continued on the development and testing of materials for various cell components, and post-test examinations of cells were made to evaluate the behavior of cell materials and to determine the causes of cell failure. Chemistry studies during the year were concerned primarily with the electrochemistry of FeS_2 and NiS_2 electrodes.

I. OVERVIEW OF BATTERY PROGRAM

The lithium/metal sulfide battery program at ANL has the dual objective of developing rechargeable batteries for use as power sources for electric vehicles and as stationary energy storage devices for load-leveling on electric utility systems. The widespread use of electric vehicles would decrease the consumption of petroleum fuels, since the energy required for charging batteries could be produced by coal, nuclear, hydroelectric, or other sources. Load-leveling batteries could also save petroleum by reducing the need for gas turbines to meet peak power demands. Stationary energy storage batteries may also find application in conjunction with solar, wind, or other cyclic or intermittent sources of energy.

Although the same electrochemical systems are being developed for these two applications and the two types of batteries share much of the same basic technology, the performance and cost goals differ significantly. Both the near- and long-term goals, which have been somewhat revised from those in last year's report, are summarized in Table 1. The electric-vehicle battery must

Table 1. Performance and Cost Goals for
Lithium/Metal Sulfide Batteries

Goal	Electric Vehicle Propulsion		Stationary Energy Storage	
	Mark I 1979	Demonstration 1983	BEST ^a 1983	Demonstration 1987
Battery Performance				
Energy Output, kW-hr	40	60	5,000	100,000
Peak Power, kW	40	60	1,500	25,000
Sustained Power, kW	16	24	1,000	10,000
Cycle Life	400	1000	500-1,000	3,000
Discharge Time, hr	4	4	5	5-10
Charge Time, hr	8	8	10	10
Cell Performance				
Specific Energy, W-hr/kg	100	160	60-80	60-150
Specific Power, W/kg	100	200	12-20	12-20
Cell Cost, \$/kW-hr	-	35-40	25-30 ^b	20

^aBattery Energy Storage Test Facility (discussed further in the text).

^bProjected cost for a production rate of 2000 MW-hr/yr.

have a high specific energy (W-hr/kg) to provide an adequate driving range, as well as sufficiently high peak and sustained specific power (W/kg) to maintain normal highway speeds and to permit passing and hill climbing. The volumetric energy and power densities (W-hr/liter and W/liter, respectively) must also be high because of the limited space available in most vehicles for installation of the battery. The specific energy and specific power requirements are less demanding for the stationary energy storage battery, whereas low cost and long lifetime are essential.

As a result of the passage by Congress of the Electric and Hybrid Vehicle Research, Development and Demonstration Act of 1976, increased emphasis has been placed on the development of the electric-vehicle battery. In November 1977, proposals were solicited for the development, design, and fabrication of a 40 kW-hr battery, designated Mark IA, to be tested in an electric van at ANL early in 1979. Two 50 kW-hr batteries, designated Mark IB and IC, will be tested approximately six and twelve months, respectively, after Mark IA. The longer-range goals for the electric-vehicle battery are listed in Table 2.

Table 2. Program Goals for Lithium/Metal Sulfide Electric-Vehicle Battery

	Mark I ^a	Mark II	Mark III	Long Range
Specific Energy, ^b W-hr/kg				
Cell (average)	100	125	160	200
Battery	75	100	130	155
Energy Density, ^b W-hr/L				
Cell (average)	320	400	525	650
Battery	100	200	300	375
Peak Power, W/kg				
Cell (average)	100	125	200	250
Battery	75	100	160	200
Heat Loss through Jacket, W	300	150	125	75-125
Lifetime				
Equivalent Full Discharges ^c	400	500	1000	1000
Equivalent Distance, km	60,000	100,000	200,000	300,000
Target Dates				
Battery Demonstration	1979	1981	1983	-
Pilot Manufacture	-	1982	1985	1990

^aGeneral goals for Mark I series batteries; the goals for the Mark IA battery are somewhat less stringent.

^bCalculated at the 4-hr discharge rate.

^cUtilization of more than 50% of the theoretical capacity every 10 cycles.

The Mark II battery will have higher performance and longer lifetime than Mark I, and will be tested in a passenger car or van in 1981. An effort will be made to keep the materials and fabrication costs as low as possible. Manufacture of Mark II batteries on pilot-plant scale by industry is currently scheduled for 1982. The Mark III battery will be designed for installation in a passenger car, and pilot-plant manufacture is expected in about 1985. The "long-range" column in Table 2 refers to the estimated performance and lifetime that can ultimately be achieved with this type of battery system.

Conceptual design studies of a battery module for stationary energy storage have been conducted at ANL and at the Atomics International (AI) Division of Rockwell International during the past year; AI and ANL are presently merging the two conceptual designs into one. Testing of this type of module in the Battery Energy Storage Test (BEST) Facility is expected to take place in 1983. The BEST Facility is a joint undertaking by the Department of Energy and the Electric Power Research Institute, and will be used to test various types of energy storage batteries on a utility system.

The ultimate goal of the program at ANL is to foster the development of a competitive, self-sustaining industry for the production of electric-vehicle and stationary energy storage batteries. To this end, industrial firms were invited to participate in the program, starting in 1975, and this arrangement is continuing, with approximately 50% of the current funding directed to industrial subcontracts. Two firms--Eagle-Picher Industries, Inc. and Gould Inc.--are developing manufacturing procedures and fabricating test cells. In addition, the Atomics International Division of Rockwell International is conducting a general research and development program with principal emphasis on lithium-silicon/iron sulfide cells and components; and Catalyst Research Corp. is investigating alternative methods of fabricating lithium-aluminum electrodes and assembly of cells in a dry room atmosphere. In the area of materials and components, the Carborundum Corporation and the University of Florida* are developing felt and paper electrode separators; Coors Porcelain and ILC Technology are developing insulated electrical feedthroughs. During the past year, the Budd Co. has conducted studies on the vehicle-battery interface and battery-configuration requirements; they have also performed experimental work on the safety aspects of lithium-aluminum/iron sulfide cells. TRW Systems, Inc. is designing a charger and cell equalization system for electric vehicle batteries. A subcontract is also in effect with Eagle-Picher for the design and fabrication of a thermally insulated jacket for preliminary tests of the lithium/metal sulfide battery. Commercialization studies have been conducted at ANL with assistance from industrial subcontractors and consultants. These studies involve the identification of potential markets, cost analyses, manufacturing and financial plans, and evaluations of competing technologies.

Engineering work at ANL includes the testing of cells fabricated by industry and development of cells and batteries. As improvements are made in the ANL cell materials and designs, they are incorporated into the cells fabricated by subcontractors. During the past year, these improvements have resulted in significant increases in the specific energy, specific power, and

* Funded directly by the Department of Energy.

lifetime of the cells. Some of the more innovative approaches to cell design that are in various stages of investigation include pellet electrodes, carbon-bonded electrodes, and new current-collector structures.

Work is continuing on the development and testing of cell materials. The use of felts or powders as electrode separators appears promising as a means of decreasing the cost and increasing the performance of cells. Development work on electrical feedthroughs has resulted in large decrease in their weight and size, along with greatly improved leak-tightness. Post-test examinations of cells have produced valuable information on the causes of cell failure. These examinations also provide data on electrode microstructure, material distribution, reaction uniformity, impurities, cross-contamination of electrodes, and corrosion rates. Cell chemistry studies during the past year were concerned mainly with lifetime-limiting mechanisms and alternative active materials for the positive electrode. Slow-sweep cyclic voltammetry has been a particularly effective technique for investigations of the electrode reactions.

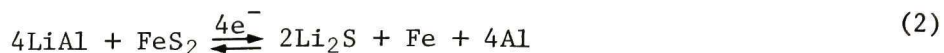
Under a separate budget activity, but closely related to the lithium/metal sulfide battery program, are continuing investigations of alternative cell systems. The objective of this work is to develop a battery that uses abundant, low-cost materials while maintaining the performance levels required for electric vehicles or load leveling. In particular, a negative electrode material less expensive and more abundant than lithium is being sought. Engineering cells having calcium-alloy negative electrodes have been operated. Investigations are also being directed toward magnesium-alloy negative electrodes.

II. CELL AND BATTERY DESIGN

The approaches taken in the design of the batteries for the electric-vehicle and stationary storage applications differ significantly. The two designs are discussed below.

A. Battery for Electric-Vehicle Propulsion

The battery cells that are currently under development have negative electrodes of lithium-aluminum alloy, positive electrodes of metal sulfide, and an electrolyte of molten LiCl-KCl eutectic. The melting point of the electrolyte (352°C) makes it necessary to operate the battery at temperatures above 400°C. In practice, the cells are assembled either in a charged, uncharged, or intermediate state. Most of the cells constructed to date are of a prismatic configuration with vertically oriented electrodes (see Fig. 1). Two negative electrodes and a central positive electrode (which usually contains transition-metal sulfide additives) are separated by a porous material such as boron nitride fabric or felt which provides electrical insulation between the electrodes and permits the migration of lithium ions through the electrolyte. Two general types of metal sulfides are being used as the active material in most positive electrodes--FeS and FeS₂. The FeS₂ electrode is capable of high specific energy and specific power, but has the disadvantages at present of limited lifetime and the requirement for expensive current-collector materials. Consequently, the FeS electrode has been selected for the first electric-vehicle battery (Mark IA). The overall reactions for cells having FeS or FeS₂ in the positive electrode are as follows:



The theoretical specific energies are about 460 W-hr/kg for Reaction 1 and 650 W-hr/kg for Reaction 2. Voltage *vs.* capacity curves show a single voltage plateau at 1.3 V for Reaction 1 and two plateaus of equal capacity at 1.7 and 1.3 V, respectively, for Reaction 2.

Figure 2 illustrates an ANL conceptual design in which a Mark I battery is installed in a van modified for electric propulsion. The two battery modules shown in the figure each have an energy output of 20 kW-hr. The Budd Co., under a subcontract with ANL, has recommended battery configurations for a modified van, a modified automobile, and an automobile designed specifically for electric propulsion. In one configuration for an advanced-design automobile, the battery housing is cylindrical and is mounted in a central tunnel of the vehicle; in another configuration the battery housing is rectangular and is an integral part of the vehicle frame.

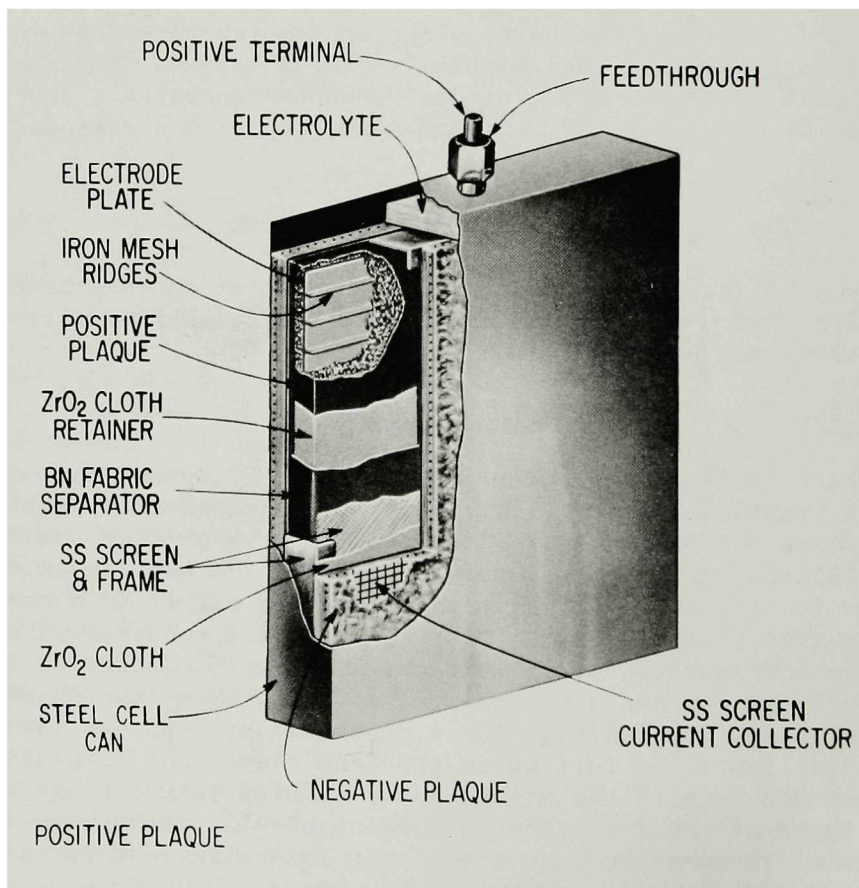


Fig. 1. Lithium/Metal Sulfide Cell

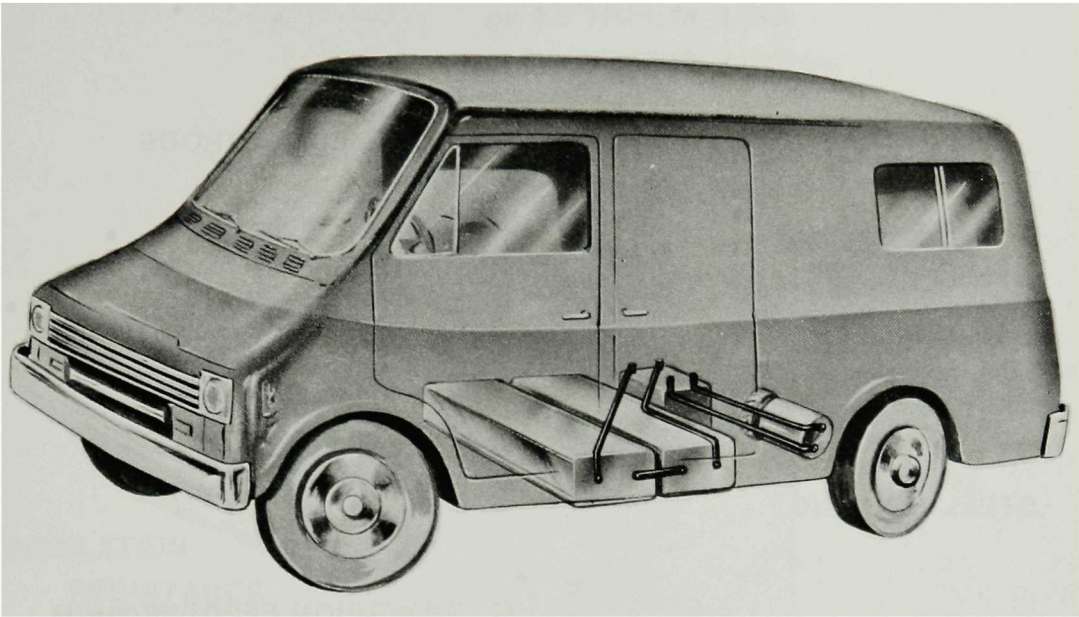


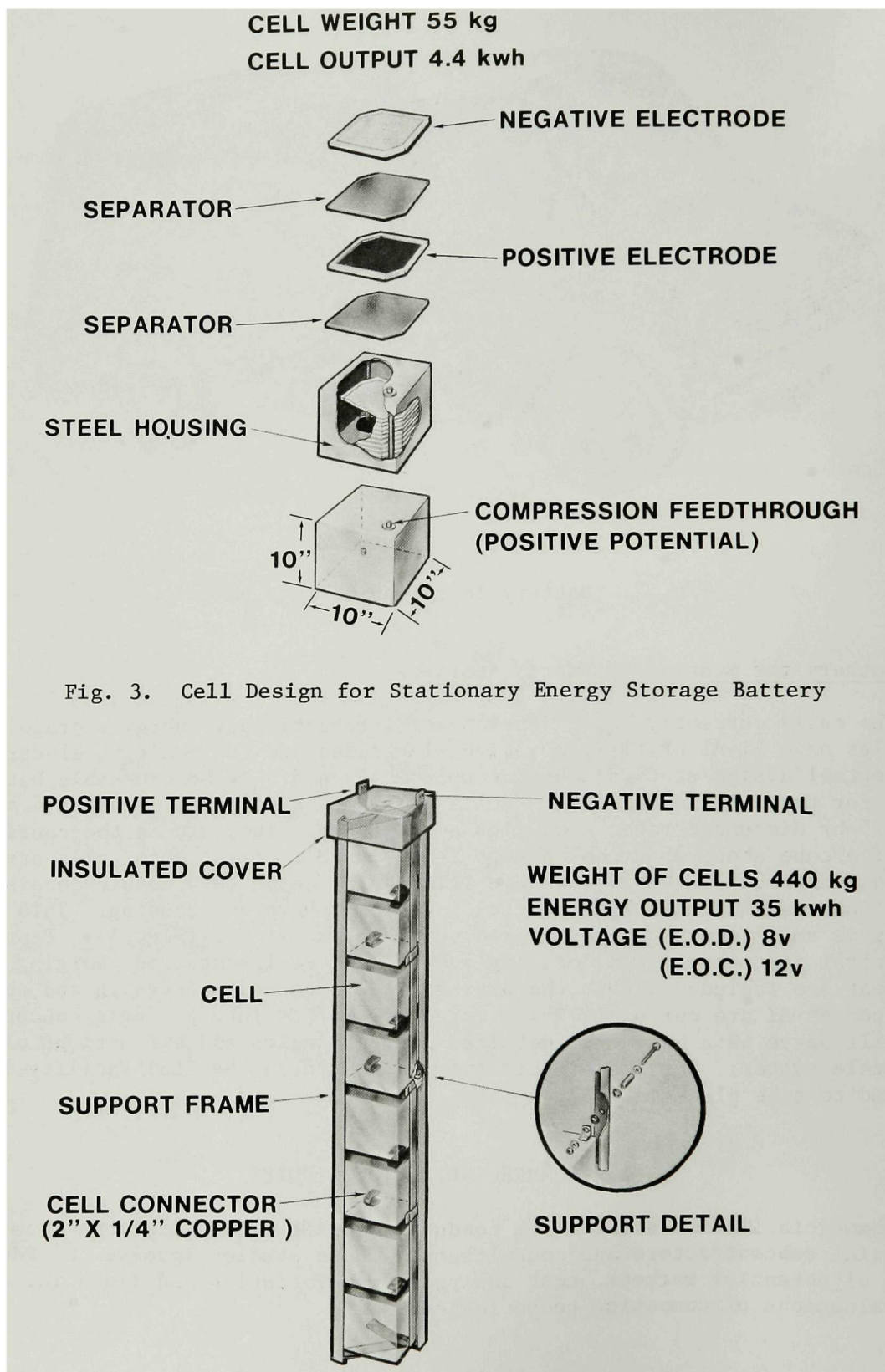
Fig. 2. Battery Installation in a Van

B. Battery for Stationary Energy Storage

The cells currently under development for stationary energy storage batteries have Li-Al or Li-Si negative electrodes and FeS positive electrodes. A conceptual design study has been completed on a 5.6 MW-hr truckable battery module for this application. The cells each have a capacity of about 4.4 kW-hr at the 5-hr discharge rate, and weigh about 55 kg. They are in the configuration of a cube about 25 cm on an edge (see Fig. 3). Eight such cells are stacked to form a 35 kW-hr submodule (Fig. 4). The battery module consists of 168 submodules, which are inserted into a weatherproof housing. This housing is small enough to be trucked to the point of use (Fig. 5). Provisions for central instrumentation, heating and cooling equipment, and charging equipment are included within the housing. This conceptual design and one developed at AI are currently being merged by AI/ANL into a single concept that will serve as a basis for detailed design studies and evaluations of a full-scale system. Testing of this type of module in the BEST Facility is expected to take place in 1983.

III. COMMERCIALIZATION STUDIES

Commercialization studies are conducted at ANL with assistance from industrial subcontractors and consultants. These studies involve the identification of potential markets, cost analyses, manufacturing and financial plans, and evaluations of competing technologies.



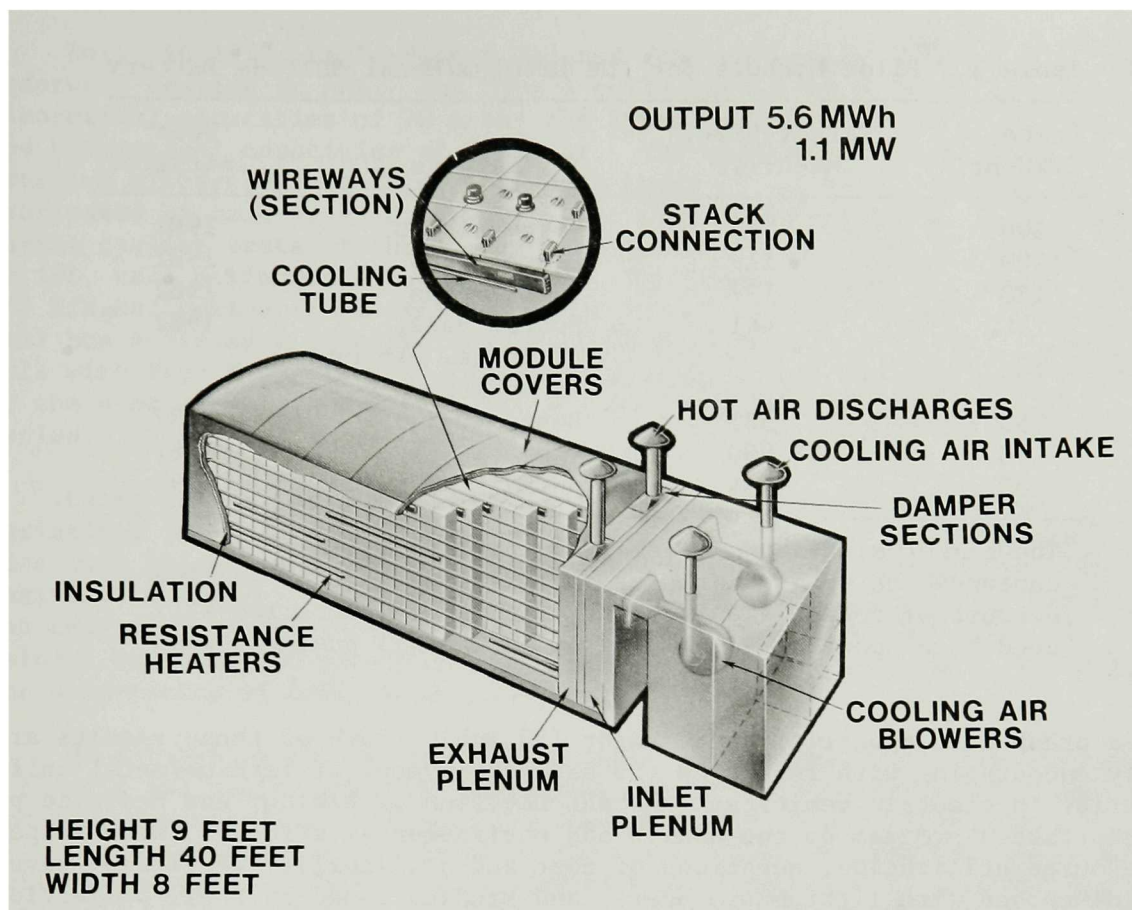


Fig. 5. Truckable Module for Stationary Energy Storage Battery

Several conditions must be satisfied to permit commercialization of the battery. A primary consideration is the technical feasibility of the lithium/metal sulfide system, and this aspect is being addressed in the research and development work. The Mark I tests of the electric-vehicle battery and the BEST Facility tests of the stationary energy storage battery are expected to establish the technical feasibility of the system. A second condition is that the battery must be marketable at an acceptable cost. The first commercial production will probably be for limited markets such as postal vans, buses, mining vehicles, and submarines. In these near-term markets the relatively high price of the batteries should be offset by their favorable performance characteristics. A study of these near-term (1982-1990) markets gave the results shown in Table 8, where the projected market size for various applications is given for different battery costs. Previous studies¹⁻³ have been conducted on the long-range, large-scale commercialization of this system, and these efforts are continuing.

The third condition that must be satisfied involves the safety aspects of the battery, environmental and health considerations, and resource utilization. A preliminary assessment on the safety aspects of the lithium/metal sulfide battery has been conducted by Budd Co. In destructive tests of cells at operating temperature (the cells were crushed and the contents exposed to air), no signs of fire or other chemical reactions were observed. Tests also indicated that the cells are capable of absorbing their own kinetic energy

Table 3. Pilot Markets for the Lithium/Metal Sulfide Battery

Price, \$/kW-hr	Market Size, ^a MW-hr/yr	Markets	Year Initiated
300	85	Submersibles	1982
200	119	Postal vans	1982
170	197	Postal vans	1982
150	441	Postal vans, buses, mining vehicles	1982
50	580	Buses	1987
50	18,900	Vans	1987
50	934	Buses	1990

^aThe market size shown assumes that the Li/MS_x battery captures the entire market. The effect of market-sharing because of competition from other advanced batteries will need to be considered as part of an overall business plan.

from a crash into a barrier at 50 km/hr (30 mph). Both of these results are highly encouraging with regard to the safe deployment of lithium/metal sulfide batteries in electric vehicles. The ANL Division of Biology and Medicine plans to undertake a program on the health and environmental effects. With respect to resource utilization, questions of cost and availability of lithium have been discussed with lithium producers, and studies based on their projections have indicated that an adequate supply will be available for at least the next twenty years at an acceptable cost.

IV. INDUSTRIAL CELL AND BATTERY TESTING

Nearly 200 cells have been fabricated by industrial subcontractors for testing at ANL or in their own facilities. These cells have a design similar to that shown in Fig. 1, and are 13 × 13 or 13 × 18 cm in the major dimensions and about 2-cm thick, with capacities in the range from 100 to 200 A-hr.

A. Testing of Industrially Fabricated Cells

Two industrial firms under contract with ANL--Eagle-Picher Industries, Inc. and Gould Inc.--are fabricating Li-Al/FeS and Li-Al/FeS₂ cells.

The main thrust of the work at Gould is the fabrication of upper-plateau* cells with FeS₂ electrodes. A cell test matrix has been devised to allow optimization of the electrode thickness and electrolyte volume for the positive electrodes, lithium content in the negative electrodes, design of the current collector, and method of particle retention. Testing of the Gould cells is being conducted both at Gould and ANL.

*These cells are operated only on the upper of two voltage plateaus that are characteristic of FeS₂ cells.

Early in 1977, Eagle-Picher FeS and FeS₂ cells that are of two thicknesses underwent testing at ANL. The Type A cells have 3.0-mm-thick electrodes* and theoretical capacities of 70 A-hr; the Type B cells have 6.0-mm-thick electrodes* and theoretical capacities of 150 A-hr. The capacities of the positive and negative electrodes are matched in both types of cells. The electrodes are fabricated by cold-pressing powders into honeycomb current collector structures. During cycling tests of these cells (hereafter referred to as baseline cells) at ANL, cell performance was measured. The baseline cell that has operated for the longest period (>998 cycles[†]) is an FeS cell with Type B electrodes. This cell has achieved a specific energy of 60 W-hr/kg at the 10-hr rate. An FeS₂ cell with Type B electrodes attained the highest specific energy (65 W-hr/kg at the 4-hr rate) and a peak specific power of 50 W/kg, with a lifetime of 525 cycles.

Later in the year, Eagle-Picher fabricated about 50 FeS and FeS₂ cells with variations in design from those of the baseline cells. These variations included electrode thickness, capacity loading of the electrodes, separator material, position of the positive terminal rod, thickness of the positive terminal rod, and design of the positive current collector. The modified cells were evaluated using a standardized procedure that permits a comparison of the performance characteristics of cells with different designs.

Of the FeS cells, the best performance was achieved by Cell I-3, which had a thinner and denser positive electrode (half-thickness, ~4.0 vs. 6.0 mm for the same capacity loading) than the Type B cell. Of the FeS₂ cells, the highest performance was achieved by Cell I-7. The positive electrode of this cell was somewhat thinner (half-thickness, ~5.0 mm) and denser (45% more active material) than the Type B electrode; the negative electrode was denser (about 50% more active material for the same thickness); and the current collector was of an improved design.[‡] Another FeS₂ cell, Cell I-6, also had very good performance characteristics. This cell design included a thinner and denser positive electrode (half-thickness, ~4.0 vs. 6.0 mm for the same capacity loading) and a denser negative electrode (about 30% more active material for the same electrode thickness) than the Type B cell.

Performance data for these three cells are presented in Table 4. For the FeS cell, I-3, the cycle life is above the goals for the cells of the Mark IA battery.** However, the specific energy and peak specific power must be

* Because the cells have two negative electrodes and one positive electrode, the positive electrode is considered to consist of two halves, each having the thicknesses given here. In the material that follows, this dimension is referred to as the half-thickness.

[†] Still in operation as of December 31, 1977.

[‡] A flexible connection between the positive terminal rod and the current collector.

** These goals are: specific energy, 80 W-hr/kg at the 4-hr rate; peak specific power, 60 W/kg; and cycle life, 200 cycles.

Table 4. Performance of Selected Eagle-Picher Cells

Cell No.	Cell Type	Specific Energy, W-hr/kg		Peak Specific Power, W/kg	Lifetime, cycles
		4-hr rate	10-hr rate		
I-3	Li-Al/FeS	50	72	36	>429 ^a
I-6	Li-Al/FeS ₂	67	85	57	133
I-7	Li-Al/FeS ₂	75	110	65	118

^aCell still in operation as of December 31, 1977.

increased. An improvement in performance is expected to be attained by further changes in cell design, such as reducing cell weight or using multiple electrodes. For the FeS₂ cell, I-7, the specific energy and peak specific power are nearly at the goals for the Mark IA battery cells, but the lifetime must be increased. The use of nickel sulfide in the positive electrode (see Section VII) may provide a means for increasing lifetime.

A facility for testing up to 100 industrial cells is presently being built in CEN; to be included as an integral part of this facility is a computer system with capabilities for automatic cycling of cells, monitoring of cell performance, and data acquisition. The facility will be used primarily for lifetime testing of industrial cells.

B. Testing of Batteries

In addition to the single-cell tests described above, the performance of cells in series and parallel arrangements is being evaluated, start-up and conditioning methods are being investigated, and various charging procedures and operational schemes are being developed. These tests are being performed using Eagle-Picher cells.

One of the batteries tested during the past year consisted of two Type B FeS cells connected in series. This two-cell battery was operated for 803 cycles and 491 days, during which time the capacity declined by 32%. Operation of the battery was terminated because a short circuit developed in one of the cells. Upon further operation of the second cell, most of its capacity was restored by increasing the operating temperature from 450 to 500°C. The effect of higher operating temperatures on performance will be investigated further.

During operation of an electric vehicle, the battery will be subjected to a variety of charge-discharge conditions. Thus, an experiment was conducted on the effect of temperature on charge and discharge, using an Eagle-Picher cell with an FeS₂ electrode. This experiment showed that a simple temperature-control and cooling system should be sufficient for an electric-vehicle battery.

An insulated case, which has reflective foil insulation in a vacuum annulus in all areas except for the front access plug, was obtained from Linde* for

* A Division of Union Carbide Corp.

testing with six Eagle-Picher cells. To permit use of this case for testing, design modifications were made to the front plug: provisions were made for current, voltage, equalization, and heater-power leads; thermocouples; and gas purge lines. In addition, internal support structures were designed for orientation, support, and clamping of the cells.

Six Type B FeS_2 cells, with mica sheets for electrical insulation, were connected in series and placed in the insulated container. The six-cell unit and the case are shown in Fig. 6. Operation of this battery revealed the need for the following: weight reduction, higher purity atmosphere, better thermal and electrical insulation, and better intercell connections. As part of the contract for the Mark IA battery, a 12-cell battery with an improved insulated case will be provided for testing at ANL. Operation of this battery will provide input data for the Mark IA design.

A facility is now being constructed for laboratory tests of large-scale (up to 60 kW-hr) electric-vehicle batteries that will precede in-vehicle tests. This facility, like the 100-cell testing facility mentioned earlier, will also have the capability for computer-controlled cell operation and data acquisition.

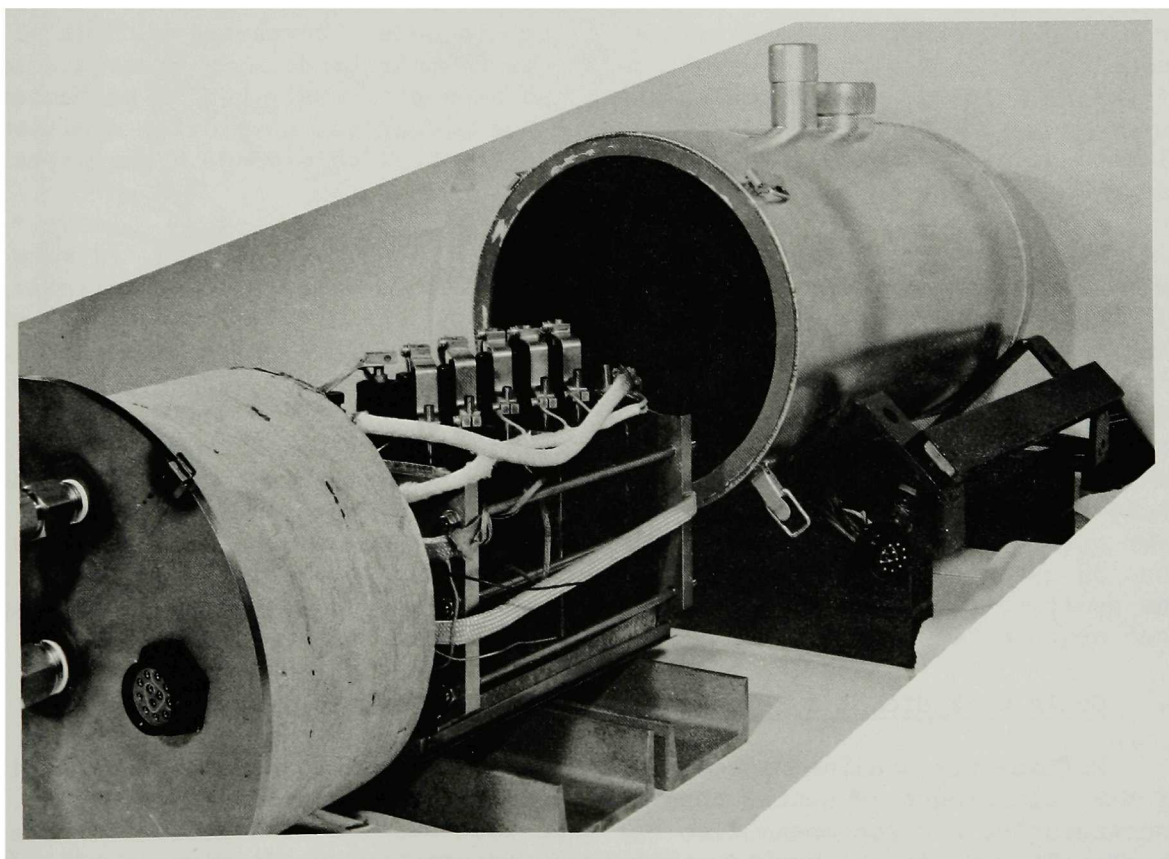


Fig. 6. Assembled Six-Cell Battery

V. CELL DEVELOPMENT AND ENGINEERING

The effort in this part of the program is directed primarily toward the development of engineering-scale, prismatic cells capable of meeting the requirements for batteries for both of our applications. Recent cell development work has concentrated on improving lifetime and specific energy at high discharge current densities ($>100 \text{ mA/cm}^2$), and on establishing improved fabrication techniques. Whenever advances in cell technology are demonstrated at ANL, these advances are incorporated as quickly as possible into the industrial cells.

Approximately 45 engineering cells were built and operated during the past year. Some of these cells are highlighted in the following discussions.

A. Cells with Iron Sulfide Electrodes

For the past several years, Cu_2S has been added to the positive electrode of Li-Al/FeS cells to eliminate the formation of J phase,* which produces diffusional overvoltage and poor electrical performance. Post-test examinations of cells of this type (Section VI.E.) have indicated, however, that cell failure is often caused by deposition of copper in the separator. For this reason, efforts are under way (1) to reduce the amount of copper in the FeS electrode or eliminate copper completely, and (2) to discover alternative methods of reducing the diffusional overvoltage of the FeS electrode. In other studies of FeS- Cu_2S cells, carbon powder which had been previously heated to temperatures above 1000°C was added to the positive electrodes to provide additional electrical conductivity. This additive is expected to produce higher specific energies in these cells.

Three charged, upper-plateau FeS_2 cells of a new design (Fig. 7) were built and operated. The essential features of this design are as follows: (1) the positive terminal rod and the honeycomb current collector, which are both made of molybdenum, are welded together; (2) the positive electrode is formed by hot-pressing a mixture of FeS_2 - CoS_2 and LiCl-KCl eutectic to the current collector; (3) the negative electrode consists of a mixture of hot-pressed Li-Al alloy and LiCl-KCl eutectic in iron honeycomb trays; and (4) double layers of Y_2O_3 or BN felt are used as the separator/particle retainer. These cells achieved very high specific energies (up to 120 W-hr/kg at the 4-hr rate[†]) owing to the compact design, but had very short lifetimes (less than 33 cycles). Modifications of the composition of the active material in the positive electrode are being made in an attempt to improve cell lifetime (see next Section).

B. Cells with Nickel Sulfide Electrodes

Voltammetry studies have indicated that the electrochemical reversibility of NiS_2 electrodes is better than that of FeS_2 electrodes (Section VII). Consequently, the recommendation was made that NiS_2 be substituted for the active material in the positive electrode or used as an additive in Li-Al/ MS_2 cells.

* $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$.

[†] Current density, 92 mA/cm^2 .

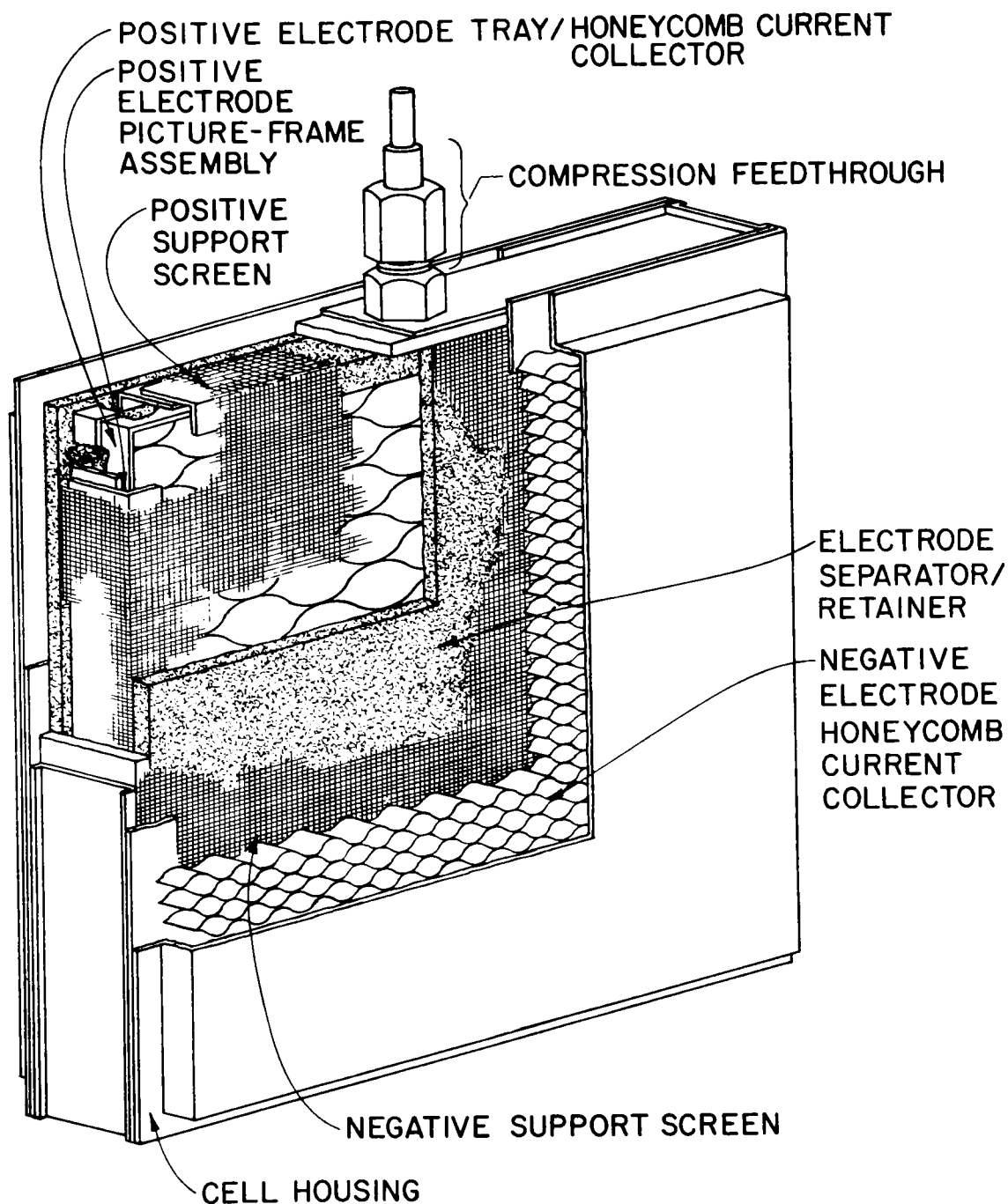


Fig. 7. Design of M-Series Cell

In the past year, four engineering-scale cells (theoretical capacities, 100-125 A-hr) with BN fabric separators and hot-pressed positive electrodes containing nickel sulfide have been tested. As can be seen from the cell data in Table 5, each of the positive electrodes has a slightly different composition of active material. The specific energies at a current density of 100 mA/cm^2 and the lifetimes of these cells are also presented in Table 5; data for a cell

Table 5. Performance of Engineering Cells
with Nickel Sulfide Electrodes

Cell No.	Positive Electrode		Specific Energy, ^b W-hr/kg	Cycle Life
	Composition of Active Material ^a	Carbon Powder Additive, wt %		
R-30	FeS _{1.65} (78.8) CoS _{1.65} (8.2) NiS _{1.65} (13.0)	10.0	50	70
R-31	NiS _{1.9} (90.7) CoS ₂ (9.3)	0	40	>200 ^c
R-32	NiS ₂ (100.0)	5.5	40	>150 ^c
R-33	NiS ₂ (50.0) FeS ₂ (50.0)	8.0	38	>90 ^c
R-26	FeS ₂ (96) CoS ₂ (4)	0	70	240

^aComposition at full charge; numbers in parentheses indicate mol % of each constituent.

^bAt a current density of 100 mA/cm².

^cStill in operation as of December 31, 1977.

with an FeS₂-CoS₂ electrode are presented for comparison purposes. Preliminary indications are that the lifetimes of cells with nickel disulfide electrodes are longer than those for cells with iron disulfide electrodes but the utilization of the active material is lower. Figure 8 depicts performance curves for a NiS₂ cell and an FeS₂ cell. Heat-treated carbon powder was added to the positive electrode of some of these cells. Further tests are needed to determine whether this additive produces the needed improvement in specific energy. Efforts are also under way to determine a positive-electrode composition that will provide optimum cell performance and lifetime.

Two other engineering cells (KK-13 and M-4) with nickel sulfide in the positive electrodes are showing promising performances. These two cells have somewhat different designs from that of the R-series cells. Both have Y₂O₃ felt separators and theoretical capacities of about 165 A-hr. The composition of the positive active material in Cell KK-13 is 88 mol % NiS₂-12 mol % CoS₂,

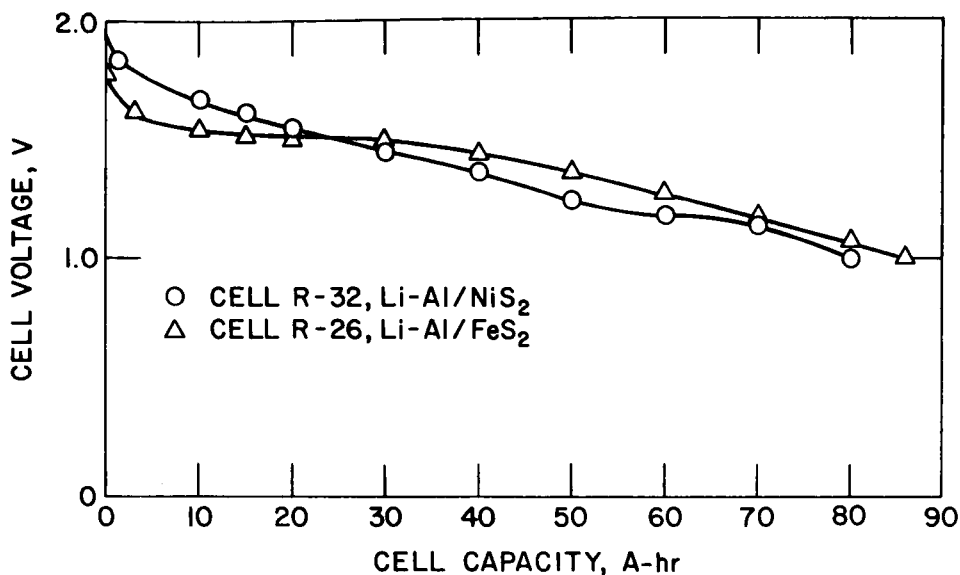


Fig. 8. Performance of Cells R-32 and R-26 (theoretical capacity: 109 and 103 A-hr, respectively) at a 15-A Discharge Current

and the positive electrode was formed by carbon-bonding.* To date, Cell KK-13 has been in operation for more than 100 cycles, and has achieved very high specific energies (70 W-hr/kg at a current density of 100 mA/cm²).

Cell M-4 has the design shown in Fig. 7. The positive active material in this cell is 69 mol % FeS_{1.46}-31 mol % NiS_{1.46}, and molybdenum powder (5.3 wt %) has been added to improve electrode conductivity. To date, Cell M-4 has operated for over 200 cycles and attained specific energies that are even higher than those of KK-13 (81 W-hr/kg at a current density of 100 mA/cm²). This cell is meeting the performance goals for the cells of the Mark IA battery.

C. Alternative Fabrication Methods

An effort is being made to develop improved fabrication procedures to reduce the cost and complexity of the cells. At present, most cells are assembled in an inert-atmosphere glove box to avoid exposure of the reactive materials to moisture and air. A fabrication method that eliminates the need for glove boxes would make cell assembly much simpler and less expensive.

A technique has been developed for assembling uncharged FeS₂ cells in air. The positive electrode is fabricated by hot-pressing Li₂FeS₂,[†] which

*The carbon-bonded electrode is formed by heat-treating a paste-like mixture of active material, a volatile constituent (ammonium carbonate) to produce porosity in the final structure, and a binder (carbon powder and furfural alcohol).

†Formed by reacting powders of Li₂S and FeS (the end products of complete discharge of FeS₂).

is relatively unaffected by air or moisture. The negative electrode is fabricated by pressing aluminum wire into sheets. Excess lithium is added to the center of this electrode in the form of lithium foil that had been previously encapsulated in aluminum foil to protect the lithium from air. The BN cloth separator is prewet by soaking it in a solution of KCl and methanol. Several engineering cells have been built by this technique. Testing of these cells has indicated that they perform similarly to cells built in a glove box. This fabrication method may be an important breakthrough for the commercialization of lithium/metal sulfide cells.

Recently, a new method of fabricating positive electrodes has been developed. This electrode is produced by hot- or cold-pressing a mixture of active material and electrolyte into a small die. The resulting structure (called a "pellet") is a durable plaque resembling a ceramic tile. Several of these pellets are then slipped into a welded grid structure of metal channels. Good electrical contact between the plaque and the current collector is made as the plaque expands during the cell reaction. This technique provides an economical, simple method for fabricating positive electrodes.

Engineering cells (both FeS and FeS₂ types) containing powder separators are also being evaluated. The powder separators replace both the BN fabric separator and the ZrO₂ cloth particle retainer, both of which are expensive. Two methods of fabrication are being evaluated: (1) hot-pressing of a ceramic-and-electrolyte powder mixture on a prepressed positive electrode and (2) vibratory filling of ceramic powder into a space between the positive and the negative electrodes. Several different powders including MgO, Y₂O₃, BN, and CaS have shown promising results.

VI. MATERIALS STUDIES

Efforts in the materials program are directed toward the development of various cell components (electrical feedthroughs, electrode separators, current collectors, and cell hardware), testing and evaluation of potential cell materials (for corrosion and wettability), and post-test examination of cells to evaluate the behavior of the electrodes and the construction materials.

A. Electrical Feedthrough Development

The design of the prismatic cell requires an electrical feedthrough to isolate the positive electrode terminal from the cell housing, which is at the negative potential. The feedthrough must be leak-tight, light in weight, inexpensive, and compatible with the cell environment. Development efforts have concentrated on two types of feedthroughs: a mechanical compression type and a brazed type.

A modified version of the Conax thermocouple feedthrough (mechanical) has been used successfully in engineering cells (greater than 1 yr of operation). Modifications involved replacing the normal sealant (lava) with BN powder and the weak lower insulator of BN with an insulator of Y₂O₃. Recently, the overall size and weight of this feedthrough have been significantly reduced by decreasing the diameter of the conductor, decreasing the length of the BN powder seal and the ceramic insulators, and replacing the large threaded nut by a snap retainer ring. An external glass seal on this feedthrough is expected to provide good

leak-tightness. The expected cost of this feedthrough is less than \$1.25/unit in quantities of about 100,000 (representing small-scale mass production). The development of the mechanical feedthrough is essentially complete; all that remains to be done is in-cell testing.

The brazed feedthrough requires corrosion-resistant, high-integrity brazed seals between the ceramic insulator and the metallic feedthrough components, conducting rod, and cell housing. To facilitate the formation of this seal, Coors Porcelain Co. developed several processes for metallizing the surfaces of Y_2O_3 ceramics. However, brazed feedthroughs proved to be unsatisfactory in in-cell tests. Current efforts at Coors Porcelain are directed toward nonmetallic brazes. The effort on the brazed feedthrough is being minimized because of the success with the mechanical feedthrough.

B. Electrode Separator Development

The primary function of the separator is to provide electrical isolation of the electrodes from each other; at the same time, it must contain sufficient electrolyte for the ready transport of lithium ions between the electrodes. A practical cell, which must be compact and lightweight, requires a porous separator that is compatible with the cell environment, permits close electrode spacing, and has low-cost potential. Candidate materials for separators* include felts, ceramic powders, and porous, sintered ceramics.

The development of BN felt separators is receiving major attention. Boron nitride felts, supplied by Carborundum Co.,[†] have shown superior performance in test cells, and have been recommended for testing in engineering cells. Cost estimates for the felts provided by Carborundum Co. range from \$13 to 19/m² (\$1.25 to 1.75/ft²), depending on thickness and density, at production rates of about 5000 kg/yr. Additional efforts are being devoted to optimizing their physical and mechanical properties.

The development of powder separators, such as AlN, MgO, and CaO, is being pursued because separators of this type facilitate cell assembly (see Section V.C.), are amenable to low-cost mass production, and permit the use of materials which are not available in fibrous form. The major disadvantage of powder separators is that they have a lower porosity than felt separators (~40 vs. ~92%), which may restrict ionic transport through the separator at high current densities. Preliminary tests of cells using MgO and Y_2O_3 powder separators have been encouraging, although they did show much lower utilizations at high current densities (120 mA/cm²) than similar cells with BN felt separators. The low projected cost of a MgO powder separator is very attractive--less than \$5.50/m² (\$0.50/ft²). Efforts are continuing on the development, characterization, and optimization of powder separators.[‡]

* In the past, BN fabric has been used successfully in engineering cells; however, the projected cost for mass production precludes its use in commercial cells.

[†] Initial development done under contract from ANL.

[‡] Development efforts are also under way at Atomics International under an ANL contract.

Porous, rigid Y_2O_3 separators with reasonable strength and porosities of about 60% have been fabricated by two techniques: (1) pressing and sintering of Y_2O_3 agglomerated particles to which organic binders have been added and (2) sintering of Y_2O_3 plaster formulations that had been cast into molds and dried. These porous Y_2O_3 separators are now undergoing cell testing. The processes described above will also be applicable to the fabrication of MgO separators. The extent of further development efforts on this type of separator will depend on results of in-cell tests.

C. Separator Wetting Studies

In the operation of a cell it is important that the separator be well wet by the electrolyte to permit easy passage of the lithium ions. Therefore, tests were conducted to determine the wettability, by molten LiCl-KCl, of candidate separator materials in porous form (*e.g.*, fabric, felt, powder). The wettability of Y_2O_3 , BN, AlN, and Al_2O_3 was determined by two methods: direct observation of the penetration of the porous material by molten salt and contact angle measurements of electrolyte drops on solid surfaces of these materials. Direct observation indicated that, in porous form, Y_2O_3 is easily penetrated by molten salt but that BN, AlN, and Al_2O_3 are difficult to penetrate. Once the latter materials are penetrated by the salt, however, they behave as wettable surfaces. The wetting characteristics of all four materials deduced from contact angle measurements were consistent with those observed in the penetration experiments.

Studies are now under way to determine pretreatment processes that will significantly improve the wettability of the separators. Preliminary results on pretreating separators with $LiAlCl_4$ have been encouraging, but additional studies are needed.

D. Corrosion Studies of Cell Materials

Corrosion testing is an integral part of the selection of suitable materials of construction for lithium/metal sulfide cells. Initial evaluations are made on the basis of static corrosion tests, and the more promising materials are sometimes tested further in specially designed test cells that simulate the environment to which a material is exposed in a practical cell. The post-test examinations of engineering cells (discussed in the following section) also provide information on corrosion behavior under actual cell operating conditions.

The search for low-cost, lightweight materials of construction for FeS and FeS_2 electrodes is being continued. Results of static corrosion tests have shown that molybdenum is the only metal that is compatible with the FeS_2 electrode; this has been confirmed by in-cell testing. For FeS electrodes, nickel and nickel-based alloys have shown good corrosion resistance; however, these materials are generally expensive. Although corrosion rates of Armco iron and low-carbon steel were high ($>400 \mu\text{m/yr}$) in static tests in an FeS environment, in-cell corrosion rates are much lower ($50\text{--}125 \mu\text{m/yr}$). Low-carbon steel has been used in all FeS cells with reasonable success. However, for long-term applications ($>5 \text{ yr}$), this material would not be satisfactory.

Because of the need for materials that are both corrosion resistant and low in cost, investigations are now being directed toward inexpensive coated materials for application in FeS_2 and FeS electrodes. Also, the search is continuing for inexpensive iron-base alloys that are compatible with FeS electrodes. Greater emphasis is being placed on in-cell corrosion testing to more clearly define the corrosion reactions and rates.

Post-test examinations of a number of cells have indicated that the Fe-Al reaction layer that is formed on cell housings and negative current collectors near the end of discharge, when the electrode is depleted of lithium, is a problem only at operating temperatures greater than 450°C , *i.e.*, above the normal cell operating temperature. When the operating temperature is kept below 450°C , the corrosion rate for the aluminum reaction with low-carbon steel is satisfactorily low (25 to $85\ \mu\text{m/yr}$).

E. Post-test Examinations

Post-test examinations are conducted on cells to determine electrode behavior (*e.g.*, electrode microstructure, reaction uniformity, and impurities), evaluate components (*e.g.*, mechanical properties and corrosion), and determine the causes of cell failure. These results are evaluated, and appropriate recommendations for improving cell performance are made to engineering personnel.

The presence of Li_2S in the separators of a number of FeS_2 cells was described in last year's report. More recent examinations have shown that a large amount of Li_2S is formed as a continuous band in the separators of all FeS_2 cells except those containing nickel and/or Hastelloy B, rather than molybdenum, current collectors. Chemical analyses of separators from FeS_2 cells with molybdenum current collectors have shown sulfur concentrations of 6 to 10 wt %, amounts that represent about 15% of the total sulfur originally in the positive electrodes. This loss of sulfur from the electrode partially accounts for the capacity decline and consequent lifetime problem of FeS_2 cells. Although the mechanism for the formation of Li_2S in the separator has not yet been identified, tests have shown that the use of a sacrificial material (*e.g.*, iron or nickel) within the electrode reduces the extent of Li_2S formation in the separator.

Microscopic examinations have shown that, upon repeated cell cycling, a connected, sponge-like microstructure is formed within Li-Al electrodes, regardless of whether the starting material is LiAl powder, aluminum wire or powder, or cast Li-Al plates. Moreover, metallographic examinations have indicated that a lithium concentration gradient occurs across the thickness of charged Li-Al electrodes. Recent ion-microprobe analyses have confirmed the existence of a gradient; lithium concentrations range from greater than 60 at. % at the front of the electrode (*i.e.*, at the face nearest the positive electrode) to less than 20 at. % at the back.

The causes of failure have been reviewed for 61 engineering cells with FeS and FeS_2 electrodes; all of these cells had vertical, prismatic designs. The results are summarized in Table 6. The following corrective actions to prevent cell failure have been recommended: (1) construction of electrode

frames with adequate strength to prevent extrusion of the active material, (2) elimination (or reduction) of the Cu_2S additive to FeS cells, and (3) addition of protective screens over honeycomb current collectors.

Table 6. Cell Failure Mechanisms

Cause of Failure	No. of Cells
Extrusion of electrode material	18
Metallic Cu in separator ^a	10
Cutting of separator by honeycomb current collector	9
Equipment malfunction ^b	7
Short in feedthrough	3
Improper cell assembly	2
Broken positive conductor	2
Unidentified	
Declining performance	7
Short circuits	3

^aFeS cell only.

^bOvercharge, temperature excursion, or polarity reversal.

VII. CELL CHEMISTRY

The cell chemistry studies are directed toward (1) solving the chemical and electrochemical problems that arise in the development of lithium/metal sulfide cells and batteries, (2) acquiring an understanding of the processes that occur within these cells, and (3) identifying new electrodes and electrolytes that may improve cell performance and life. Most of the cell chemistry studies this year were concerned with the properties of metal disulfide electrodes.

Slow-scan cyclic voltammetry has been used to elucidate the charge and discharge reactions of the FeS_2 electrode *vs.* LiAl (45 at. % Li) in LiCl-KCl electrolyte. A typical voltammogram is given in Fig. 9 (charge reactions are shown above the horizontal line and discharge reactions below). Poor electrochemical reversibility is indicated by the large voltage separation between the major charge and discharge reactions in the high-voltage region (1.5 to 2.0 V). The major discharge peak begins at 1.74 V, which is the potential observed on the upper voltage plateau of Li-Al/FeS_2 cells; however, the major charge peak begins at 1.86 V, which is close to the potential required for oxidation of Li_2S to sulfur.

Metallographic studies indicate that this charge reaction proceeds by formation of an electrolyte-soluble, sulfur-rich species that reacts with Fe_{1-x}S to form FeS_2 . Thermodynamic calculations indicate that FeCl_2 , an

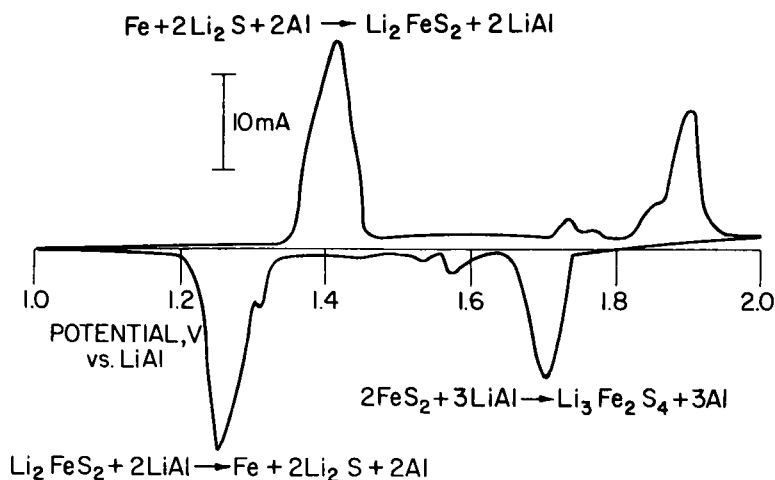
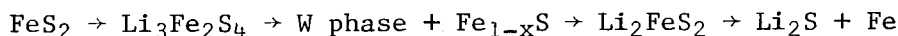


Fig. 9. Voltammogram for FeS_2 in LiCl-KCl Electrolyte at 405°C (scan rate, 0.015 mV/sec)

electrolyte-soluble iron species, also forms during this reaction. It is possible that these soluble sulfur and iron species diffuse from the positive electrode and are reduced as they approach or contact the negative electrode. Thus, the unacceptable amounts of Li_2S and iron that have been found in the BN separators of FeS_2 -type cells (Section VI.E.) may be a consequence of the poor charge kinetics of FeS_2 .

The labelled reactions in Fig. 9 were identified in phase studies using metallographic and X-ray techniques. These studies showed that the discharge of FeS_2 in Li-Al/LiCl-KCl/ FeS_2 cells gives the following sequence of products:



The composition of the W phase has not yet been determined, and only the first and last reactions in the above sequence give rise to major discharge peaks. The intermediate products, W phase and Fe_{1-x}S , exist in the region between the two major discharge peaks, and are also present in the region between the major charge peaks. The conversion of these intermediate products to FeS_2 during charge probably occurs through the formation of soluble species as described in the preceding paragraph.

In a search for electrodes having better electrochemical reversibility than FeS_2 , NiS_2 was investigated by cyclic voltammetry. As can be seen from Fig. 10, this electrode has excellent electrochemical reversibility. Tests of NiS_2 (and of NiS_2 - FeS_2 mixtures) in engineering cells suggest that the lifetime-limiting mechanisms encountered with FeS_2 electrodes are absent in the electrodes that contain nickel (see Section V.C.).

The study of TiS_2 as an alternative positive-electrode material, which was started last year, has been continued. Preliminary tests were conducted with LiAl/ TiS_2 cells having capacities of 75 to 140 A-hr. Although specific energies of 67 and 46 W-hr/kg were achieved at the 10- and 4-hr rates,

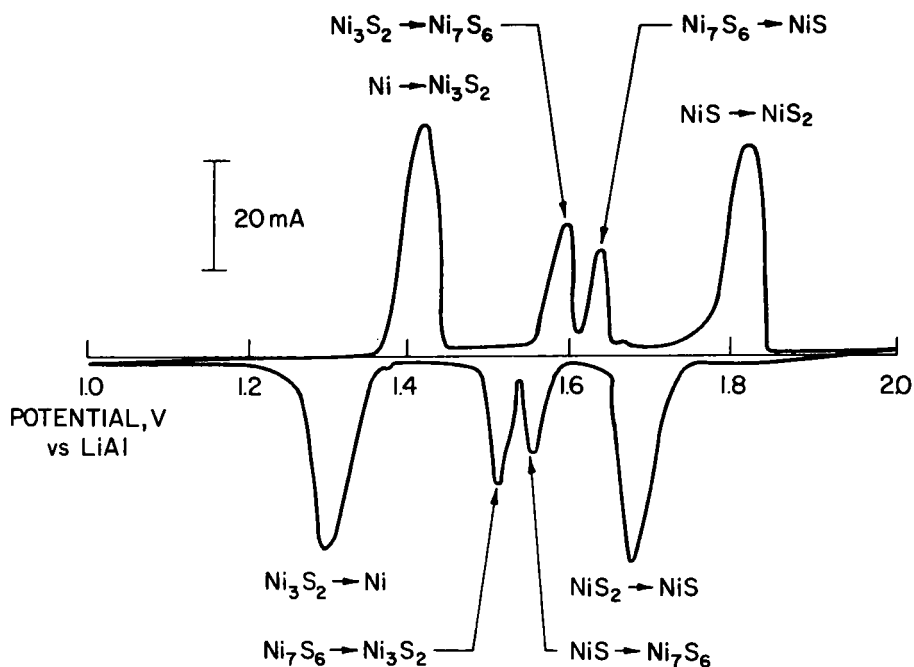


Fig. 10. Voltammogram for NiS_2 in LiCl-KCl Electrolyte at 405°C (scan rate, 0.015 mV/sec)

respectively, a variety of mechanical problems led to short-circuiting during the first 20 cycles of operation.

Future work in cell chemistry will be devoted to attaining a more complete understanding of the properties of FeS_2 electrodes and to finding methods of improving electrochemical reversibility. Methods of improving the performance of the other metal sulfide electrodes that are now being developed at ANL (*i.e.*, NiS_2 , TiS_2 , FeS) will also be investigated, and the search for new positive electrodes will continue.

VIII. ALTERNATIVE CELL SYSTEMS

The purpose of this work is to develop a molten-salt secondary cell using negative electrode material that is less expensive and more abundant than lithium. Calcium/metal sulfide and magnesium/metal sulfide cells are being investigated because their theoretical specific energies are comparable to those of analogous lithium/metal sulfide cells. The near-term goal of this research is to demonstrate a cell performance approaching that of lithium/metal sulfide cells; the long-term goal is to produce new, low-cost batteries that will have the cycle life and performance required for electric-vehicle and stationary energy storage applications.

During the past year, candidates for positive electrodes in calcium and magnesium cells were investigated. Studies indicated that, of the transition-metal sulfides, only the sulfides of nickel have acceptable performance and resistance to overcharge in calcium cells. In magnesium cells, NiS_2 and possibly TiS_2 are acceptable positive electrodes.

Of the two types of cells under investigation, the calcium systems are the most advanced; Ca-(Mg₂Si)/NiS (or NiS₂) cells have demonstrated reasonably good capacity densities of 0.3 A-hr/cm² in small cell tests (up to 5 A-hr capacity). However, in engineering cells (about 100 A-hr capacity), capacity densities of only 0.1 A-hr/cm² (about 30% electrode utilization) have been achieved. A recent post-test examination has suggested that this poor capacity density resulted from a reaction of calcium with the ZrO₂ fabric which was used as a particle retainer. Cells are now being fabricated without ZrO₂ fabric retainers to determine the effect on cell performance.

Tests of small magnesium/metal sulfide cells have shown that they are electrochemically reversible. A problem that continues to prevent scale-up of magnesium cells is the formation of dendritic magnesium deposits on magnesium and its alloys (Mg-Al and Mg-Pb alloys, for example). These dendrites grow on the negative electrode and penetrate the separator, thereby causing a short circuit. Production of a successful magnesium secondary cell depends on finding a solution to this problem.

None of the calcium or magnesium cells tested so far have performed as well as the lithium/metal sulfide cells. Studies in the coming year will be directed toward improving the performance of these cells and investigating the properties of other types of positive electrodes, such as metal oxides or metal halides.

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